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EP 0190814 A US 4743499 A
US 4668564 A
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(54) Abstract Title

Layered materials

(57) The invention provides a layered material comprising a hydrophilic foam layer formed from a first polyurethane and a hydrogel layer formed from a second polyurethane, wherein the hydrogel layer is laminated to the hydrophilic foam layer. The invention also provides wound dressings comprising the layered materials. The invention also provides methods for preparing the layered materials comprising the steps of: providing a first, foamed polyurethane layer by reacting a first isocyanate-capped prepolymer with water; and providing a second, hydrogel polyurethane layer by reacting a second isocyanate-containing prepolymer with a crosslinking agent, wherein the second layer is applied to the first layer before said steps of reacting are complete, whereby urethanes or urea cross-links are formed between the foamed polyurethane layer and the hydrogel polyurethane layer.

FIG. 1

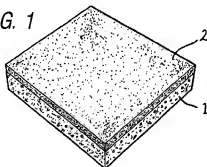
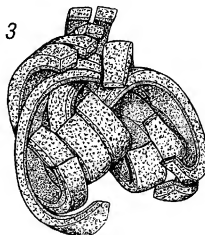


FIG. 3



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FIG. 1

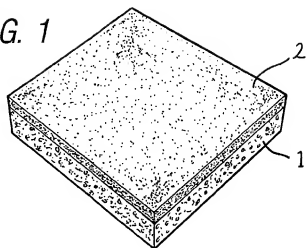


FIG. 2(a)

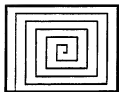
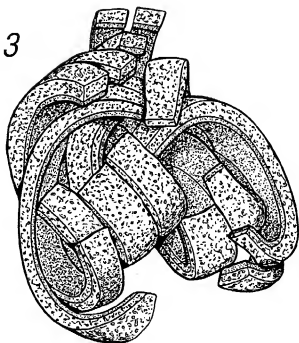


FIG. 2(b)



FIG. 3



LAYERED MATERIALS

The present invention relates to layered polyurethane materials, especially for use as or in wound dressings.

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EP-A-0541391 describes hydrophilic polyurethane foams for use as absorbent and wound contacting layers in wound dressings.

It is also known to provide wound dressings in which the wound contacting
10 layer comprises a polyurethane hydrogel material especially suitable for absorbing
bodily fluids such as wound exudate. For example, US-A-5160328 describes such
a dressing having a wound contacting polyurethane hydrogel layer. The
polyurethane gel comprises from 0% to 90% of polyhydric alcohol such as
polypropylene glycol, from 6% to 60% by weight of an isocyanate-terminated
15 prepolymer, from 4% to 40% by weight of a polyethylene oxide based diamine,
and the balance water. The hydrogel layer is disposed on a support layer that
provides mechanical support for the relatively weak hydrogel.

Hydrogel dressings are advantageous because wound exudate does not
20 generally dry and consolidate with hydrogels. Consequently, the removal of a
hydrogel dressing is usually neither painful nor detrimental to the healing process.
Hydrogel dressings are particularly desirable for the treatment of burns.

Unfortunately, hydrogel dressings have limited capacity to absorb further
25 water. Furthermore, there are difficulties in handling the structurally weak gels in
high speed manufacturing processes. This has been addressed in US-A-5160328
by the provision of a support layer underneath the hydrogel layer, but it is difficult
to achieve satisfactory adhesion of the hydrogel layer to the support layer.

30 EP-A-0610056 describes a hydrogel dressing which comprises a wound
contacting layer of hydrogel in face-to-face relationship with a substrate. The
hydrogel facing surface of the substrate comprises fibers projecting into the
hydrogel. The hydrogel is cross-linked on the substrate and thereby firmly

anchored thereto. The preferred hydrogel for use in this invention is polyvinylpyrrolidone, which is cross-linked by irradiation.

EP-A-0604103 describes processes by which a polymeric hydrogel can be
5 securely adhered to a substrate to form a hydrogel laminate with greatly improved delamination resistance. The laminate is formed by casting onto a polymeric adhesive-coated substrate an aqueous solution of hydrophilic polymer, then exposing this composite to ionizing radiation which cross-links the hydrophilic polymer to form a hydrogel and also induces copolymerisation of the hydrophilic
10 polymer and the adhesive polymer.

It has now been found that novel composite polyurethane structures provide a hydrogel layer with enhanced rigidity, delamination resistance and liquid absorbency.

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The present invention provides a layered material comprising a hydrophilic foam layer formed from a first polyurethane and a hydrogel layer formed from a second polyurethane, wherein the hydrogel layer is laminated to the hydrophilic foam layer.

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Preferably, the hydrophilic foam layer has a density of from 0.28 to 0.5 g/cm³, and more preferably from 0.32 to 0.48 g/cm³. Preferably, the foam has an elongation to break of at least 150%, more preferably from 500% to 1000%. The foam is hydrophilic and absorbs aqueous fluids such as wound exudate with
25 swelling. However, the foam is preferably highly cross-linked and substantially insoluble in water. Preferably, the foam has an absorbency of at least 3 g saline/g, and preferably a swellability in water of at least 200%. Preferably, the hydrophilic foam is a foam as described in EP-A-0541391, the entire content of which is incorporated herein by reference.

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Preferably, the foamed polyurethane layer comprises less than 10% water prior to use as an absorbent, more preferably less than 5% water and more preferably it contains less than 2% of water before use.

- The hydrophilic foam provides enhanced absorbency for liquid exudate. This is because the initial substantially anhydrous condition and porous structure of the foam enable it to absorb a larger amount of water by both chemical and physical absorption that is the case for the corresponding hydrogel material.
- 5 Furthermore, the porous structure of the foam provides for rapid uptake of liquid exudate, in contrast to pure hydrogel dressings. Preferably, the hydrophilic foam layer has a thickness of from 1 to 20 mm, more preferably from 1.5 to 5 mm.

- The hydrogel layer is formed from a polyurethane that entraps water to form
- 10 a gel. Preferably, the hydrogel layer is substantially continuous, and preferably it is substantially non-porous. Preferably, the density of the hydrogel layer is greater than 0.5 g/cm^3 , more preferably greater than 0.8 g/cm^3 , and most preferably from 0.9 to 1.1 g/cm^3 . Preferably, the thickness of the hydrogel layer is from 1 mm to 10 mm, more preferably from 2 mm to 5 mm.

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- Preferably, the polyurethane of the hydrogel layer is cross-linked and preferably it is substantially insoluble in water at ambient temperature. However, the structure of the hydrogel layer absorbs and entraps water to provide a highly hydrated gel structure in contrast to the porous foam structure of the foam layer.
- 20 Preferably, the gel can absorb 1 to 10 g/g of physiological saline at 20° , more preferably 2 to 5 g/g. The saline absorbency is determined by the steps of: weighing the hydrogel, submerging the hydrogel in 0.9% saline for 24 hours, draining for 30 seconds, and reweighing.

- 25 Preferably, the dry weight of the hydrogel layer is from 1000 to 5000 g/m^2 , more preferably from 2000 to 4000 g/m^2 . Preferably, the hydrogel comprises from 1 to 30% of water, more preferably from 10 to 20% by weight of water before use. Preferably, the hydrogel contains from 1 to 40%, more preferably from 5 to 15%, by weight of one or more humectants, preferably selected from the group
- 30 consisting of glycerol, propylene glycol, sorbitol, mannitol, polydextrose, sodium pyrrolidine carboxylic acid (NaPCA), hyaluronic acid, aloe, jojoba, lactic acid, urea, gelatin, lecithin and mixtures thereof. The entrapped water and optional

humectants give the hydrogel a soft, moist wound-friendly surface for contacting the wound.

The hydrogel layer is laminated to the foam layer. That is to say, it is applied to and at least partially covers one surface of the foam layer. Preferably, the hydrogel layer is bonded to the foam layer, for example by an adhesive or by radiation cross-linking. More preferably, the hydrogel layer is bonded to the foam layer by urethane or urea linkages. This can be achieved easily by applying the foam layer to the hydrogel layer (substantially without mixing) before polyurethane curing is complete, as described in more detail below.

Preferably, the foam layer polyurethane and/or the hydrogel layer polyurethane are formed by crosslinking an isocyanate-capped prepolymer. Preferably, the prepolymer is the same for both layers. Preferably, the prepolymer comprises an isocyanate-capped polyether prepolymer, and more preferably it comprises an isocyanate-capped ethyleneoxy/propyleneoxy prepolymer. For example, one of the prepolymers available under the Registered Trade Mark HYPOL from Dow Chemical Company, 2 Heathrow Boulevard, 284 Bath Road, West Drayton, UK.

Preferably, the foam layer and/or the hydrogel layer contains a medicament. Suitable medicaments include antiseptics such as silver sulfadiazine, chlorhexidine, triclosan or povidone iodine, analgesics, steroids, antibiotics, growth factors or mixtures thereof. Preferably, the layered material is substantially sterile.

The present invention also provides a wound dressing comprising a layered material according to the invention as hereinbefore described.

Preferably, the wound dressing further comprises a liquid-impermeable backing sheet extending over the laminated material. Preferably, the backing sheet is a semipermeable sheet, for example a sheet of a microporous polyurethane foam such as ESTANE (Registered Trade Mark). Preferably, the backing sheet is provided with a continuous or interrupted layer of a pressure-

sensitive adhesive, preferably one of the known medical-grade adhesives. Preferably, an adhesive-coated margin of the backing sheet extends beyond at least one edge of the laminated material for attachment of the backing sheet to the skin of a patient adjacent to a wound under treatment. More preferably, an
5 adhesive-coated margin of the backing sheet extends around all edges of the layered material so as to provide a so-called island dressing.

The backing sheet may be provided on either the foam side of the layered material or on the hydrogel side. Intermediate layers, such as absorbent layers or
10 support layers, may be provided between the layered material and the backing sheet.

The layered material is usually provided in substantially flat sheet form for topical application to wounds. However, the layered material may be contoured for
15 application to body surfaces having high curvature. In certain preferred embodiments the layered material is formed into a three-dimensional shape for deep cavity wound filling. For example, the layered material may be folded or crumpled. Preferably, a deep cavity wound dressing comprises entangled strips of the layered material.

20 The present invention further provides the use of a layered material according to the invention for the preparation of a dressing for use in the treatment of wounds. Preferably, the dressing is in accordance with one of the above-described embodiments

25 In a further aspect, the present invention provides a method of treatment of a wound comprising applying a wound dressing according to the present invention to the surface of the wound with the foam layer or the hydrogel layer of the layered material in liquid communication with the wound, and preferably in contact with the
30 wound, to absorb wound exudate.

The present invention further provides a method of preparing a layered structure comprising the steps of: providing a first, foamed polyurethane layer by

reacting an isocyanate-capped prepolymer with water and optionally one or more compounds selected from polyurethane chain extending or terminating compounds other than water and catalysts for the polymerisation of isocyanate; providing a second, hydrogel polyurethane layer by reacting an isocyanate-
5 containing prepolymer with one or more compounds selected from water, other polyurethane chain extending or terminating compounds and catalysts for the polymerisation of isocyanate; and laminating the second layer to the first layer.

Preferably, the layered structure prepared by the method of the invention is
10 a layered structure according to the invention as hereinbefore described.

Preferably, the first layer is laminated to the second layer before the steps of reacting are complete, whereby urethane or urea linkages are formed between the foamed polyurethane layer and the hydrogel polyurethane layer.

15 Preferably, the method further comprises the step of drying the polyurethane foam layer, preferably after the step of laminating.

Preferably, the prepolymer is the same for both layers. Preferably, the prepolymer comprises an isocyanate-capped polyether prepolymer, and more
20 preferably it comprises an isocyanate-capped ethyleneoxy/propyleneoxy prepolymer. For example, one of the prepolymers available under the Registered Trade Mark HYPOL from Dow Chemical Company, 2 Heathrow Boulevard, 284 Bath Road, West Drayton, UK.

25 Preferably, the chain terminating compounds comprise a monoamine or a monohydric alcohol, more preferably a C₁ to C₃ alcohol, and most preferably methanol. In certain preferred embodiments of the foam preparation, one part of the prepolymer is reacted with water in the presence of from 0.05 to 0.25 parts by weight of methanol or from 0.1 to 0.3 parts by weight of ethanol. The amounts of
30 chain terminating compounds influence the physical properties of the polyurethane foam or gel. For example, the tackiness of the polyurethane increases with increasing monohydric alcohol or monoamine content.

Preferably, the chain extending compounds comprise water or a diamine. Reaction with water produces carbon dioxide for foaming and urethane cross-links. Reaction with diamines, which takes place much faster than reaction with water, gives urea cross-links. Preferred diamines include C₃ to C₉ alkylene diamines such as hexamethylene diamine.

Preferably, the step of providing the polyurethane foam layer comprises: mixing 1 part by weight of an isocyanate-capped prepolymer having from 0.5 to 1.2 meq NCO groups/g with from 0.4 to 1.0 parts by weight of water in the presence of from 0.05 to 0.4 parts by weight of a C₁ to C₃ monohydric alcohol.

Preferably, the method of the invention further comprises the step of slitting the layered material before the steps of reacting or curing of the polyurethanes are complete to provide a plurality of linked strips of the layered material. As curing and drying proceeds, the strips curl and entangle as a result of differential shrinkage rates in the foam and hydrogel layers. This can result in a three-dimensional bundle of strips suitable for use as a deep cavity wound dressing.

Specific embodiments of the invention will now be described further, by way of example, with reference to the accompanying drawings, in which:

Figure 1 shows a perspective view of a flat layered material according to the present invention; and

Figure 2 shows a plan view of two alternative patterns of full thickness slits formed in a laminate prior to final curing and drying in order to achieve a deep cavity dressing; and

Figure 3 shows a perspective view of a deep cavity wound dressing formed from layered material in accordance with the invention.

Example 1

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A layered material is prepared from the following constituents:

Foam Layer:	HYPOL ^a	50g
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	Water	32g
	Acrylic copolymer ^b	12g
	Methanol	6g
5	Hydrogel Layer	
	HYPOL ^a	25g
	Water	100g

^a HYPOL PreMA G60 from Dow Corning Ltd.

^b PRIMAL B-15J or RHOPLEX N-560 (Registered Trade Marks).

- 10 The components of each layer are mixed and spread individually to make flat sheets of nominal thickness 1 to 5 mm. The sheets are allowed to cure partially for about 90 seconds at ambient temperature, and are then pressed gently together and placed in an oven at 100°C for about 15 minutes to complete the curing and drying.

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The resulting laminate, which is shown in Figure 1 has a polyurethane foam layer 1 laminated to a hydrogel wound contacting layer 2.

Example 2

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A deep cavity wound dressing is prepared as follows.

- 25 The procedure of Example 1 is followed with the additional step of slitting the laminate in dendritic or spiral fashion as shown in Figure 2 before the final oven curing and drying step. The process includes an additional drying and curing step at 40°C for about 30 minutes. The strands of the laminate curl and entangle during the final curing and drying step to produce the three-dimensional deep cavity dressing shown in Figure 3.

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The above embodiments have been described by way of example only. Many other embodiments falling within the scope of the accompanying claims will be apparent to the skilled reader.

CLAIMS

1. A layered material comprising a hydrophilic foam layer formed from a first polyurethane and a hydrogel layer formed from a second polyurethane, wherein
5 the hydrogel layer is laminated to the hydrophilic foam layer.
2. A layered material according to claim 1, wherein the hydrophilic foam layer has a density of from 0.28 to 0.5 g/cm³.
- 10 3. A layered material according to claim 1 or 2, wherein the hydrophilic foam layer has a thickness of from 1 to 20 mm.
4. A layered material according to any preceding claim, wherein the hydrogel layer is substantially unfoamed.
- 15 5. A layered material according to any preceding claim, wherein the dry weight of the hydrogel layer is from 1000 to 5000 g/m².
6. A layered material according to any preceding claim, wherein the hydrogel
20 layer is bonded to the foam layer by urethane or urea linkages.
7. A layered material according to any preceding claim, wherein the foam layer polyurethane and/or the hydrogel layer polyurethane are formed by crosslinking an isocyanate-capped prepolymer.
- 25 8. A layered material according to claim 7, wherein the prepolymer comprises an isocyanate-capped polyether prepolymer.
9. A layered material according to claim 8, wherein the prepolymer comprises
30 an isocyanate-capped ethyleneoxy/propyleneoxy prepolymer.

10. A layered material according to any preceding claim wherein the hydrogel layer comprises from 10 to 30% by weight of water and the foam layer comprises less than 10% by weight of water.
- 5 11. A layered material according to any preceding claim which is substantially sterile.
12. A layered material according to any preceding claim, wherein the foam layer and/or the hydrogel layer contains a medicament.
- 10 13. A wound dressing comprising a layered material according to any one of claims 1 to 12.
14. A wound dressing according to claim 13, further comprising a liquid-impermeable backing sheet extending over the laminated material.
- 15 15. A wound dressing according to claim 3, wherein the layered material is formed into a three-dimensional shape for deep cavity wound filling.
- 20 16. A wound dressing according to claim 15, wherein the wound dressing comprises entangled strips of the layered material.
17. Use of a layered material according to any one of claims 1 to 12 for the preparation of a dressing for use in the treatment of wounds.
- 25 18. A method of preparing a layered structure comprising the steps of:
providing a first, foamed polyurethane layer by reacting an isocyanate-capped prepolymer with water and optionally one or more compounds selected from polyurethane chain extending or terminating compounds other than water
30 and catalysts for the polymerisation of isocyanate;
providing a second, hydrogel polyurethane layer by reacting an isocyanate-containing prepolymer with one or more compounds selected from

water, other polyurethane chain extending or terminating compounds and catalysts for the polymerisation of isocyanate; and
laminating the second layer to the first layer.

5 19. A method according to claim 18, wherein the layered structure is a layered structure according to any one of claims 1 to 12.

20. A method according to claim 18, wherein said first layer is laminated to said second layer before said steps of reacting are complete, whereby urethane or
10 urea linkages are formed between the foamed polyurethane layer and the hydrogel polyurethane layer.

21. A method according to any one of claims 18 to 20, further comprising the step of drying the polyurethane foam layer after said step of laminating.

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22. A method according to any one of claims 18 to 21, wherein the chain terminating compounds comprise a monohydric alcohol.

23. A method according to any one of claims 18 to 22, wherein the chain
20 extending compounds comprise a diamine.

24. A method according to any one of claims 18 to 22, wherein the step of providing the polyurethane foam layer comprises: mixing 1 part by weight of an isocyanate-capped prepolymer having from 0.5 to 1.2 meq NCO groups/g with
25 from 0.4 to 1.0 parts by weight of water in the presence of from 0.05 to 0.4 parts by weight of a C₁ to C₃ monohydric alcohol.

25. A method according to any one of claims 20 to 24, wherein the prepolymer comprises an isocyanate-capped polyether prepolymer.

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26. A method according to claim 25, wherein the prepolymer comprises an isocyanate-capped ethyleneoxy/propyleneoxy prepolymer.

27. A method according to any one of claims 20 to 26, wherein the same isocyanate prepolymer is used to prepare both the foam layer and the hydrogel layer.

- 5 28. A method according to any one of claims 20 to 27, further comprising the step of slitting the layered material before curing and drying of the polyurethane layers are complete to provide a plurality of linked strips of the layered material.



INVESTOR IN PEOPLE

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Claims searched: 1-28

Examiner: Richard Gregson
Date of search: 22 May 2001

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.S): B5N

Int Cl (Ed.7): A61F (13/02), A61L (15/26), B32B (5/18, 27/40), C08L (75/04)

Other: Online: EPODOC, WPI, JAPIO, RM25

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	EP 0190814 A (SQUIBB) - see diagrams, abstract and pages 7-9 in particular.	n/a
A	US 4743499 A (VOLKE) - see whole document.	n/a
X	US 4668564 A (ORCHARD) - see diagrams, column 2, lines 25-29 and column 4 in particular.	1,4,6,7,1,1 8,201 at least
X	WPI Abstract, Acc. No. 1992-128775 & JP 4073011 (FRANCE BED KK) - see diagrams and abstracts.	1

X Document indicating lack of novelty or inventive step
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